Fly Ash Catalyzed Mercury Oxidation Chlorination Reactions

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Introduction

- Strict EPA regulations for mercury control.
- Mercury control depends on the speciation of mercury.
- Gas phase reactions don't influence the effluent mercury speciation.
- Surface reactions in the post combustion zone control mercury speciation in stack gases.
- Surface composition plays an important role in mercury transformation.
- Study of mercury transformation in the post combustion zone is important to determine the speciation of mercury.

Possible Mercury Transformation Reactions in Combustor Cool Zone

- Oxidation
  - Activated Carbon
  - Fly Ash
  - Surface Oxygen Complexes
- Chlorination
  - HCl (poor chlorinating agent)
  - Conversion of HCl to Cl_2 (Deacon Reaction)
  - Role of Metals

Role of Surfaces

- Adsorption

- Dependence on carbon/calcium content

- Catalysis

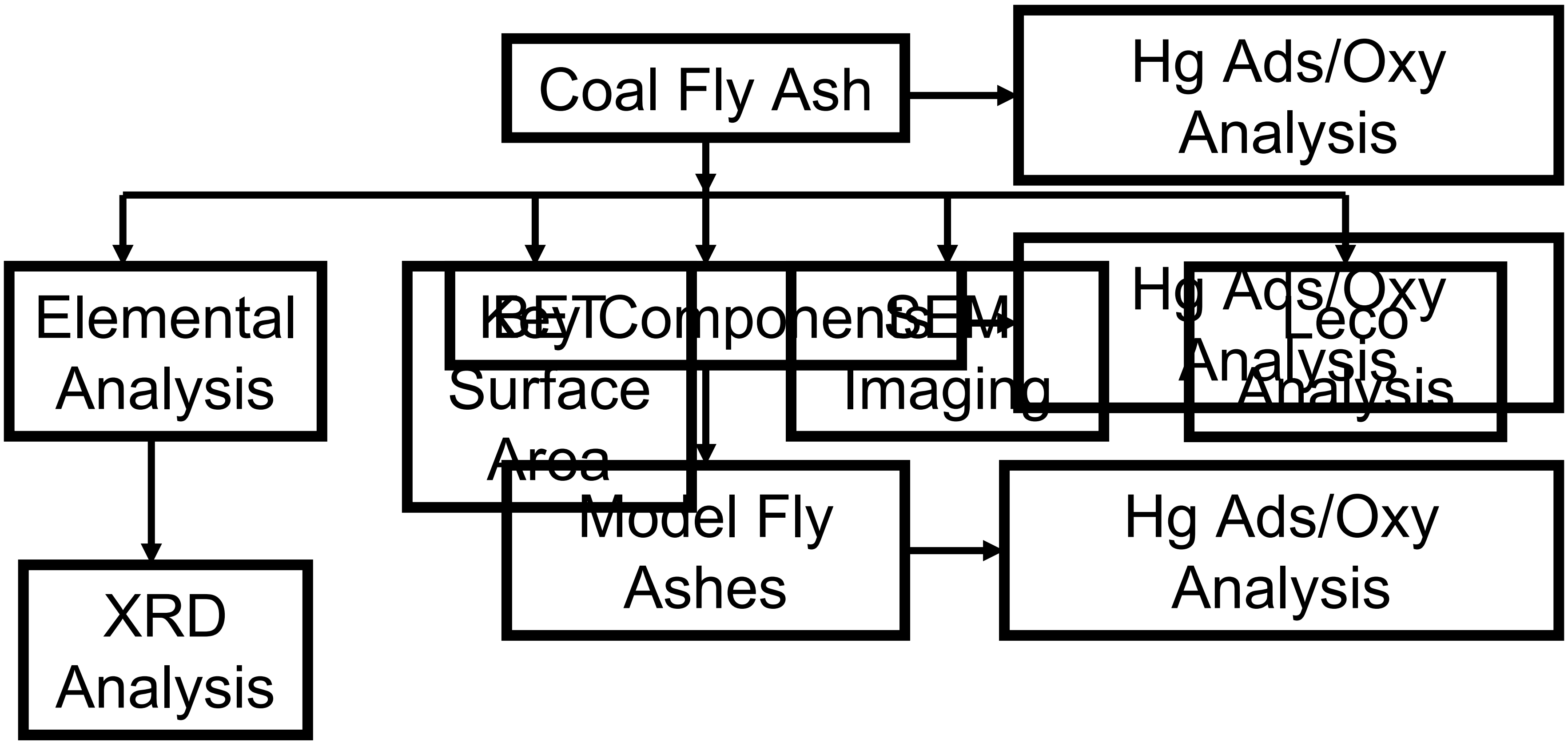
- Dependence on metal content

Surfaces play an important role in mercury transformation reactions

Objectives

- Understand how fly ash surface and composition of flue gas affect mercury speciation, partitioning, and reactions under post-combustion zone conditions.
- Use this knowledge to develop a predictive tool that could estimate mercury speciation based on fly ash characteristics and composition of flue gas.

Experimental Approach: Surface

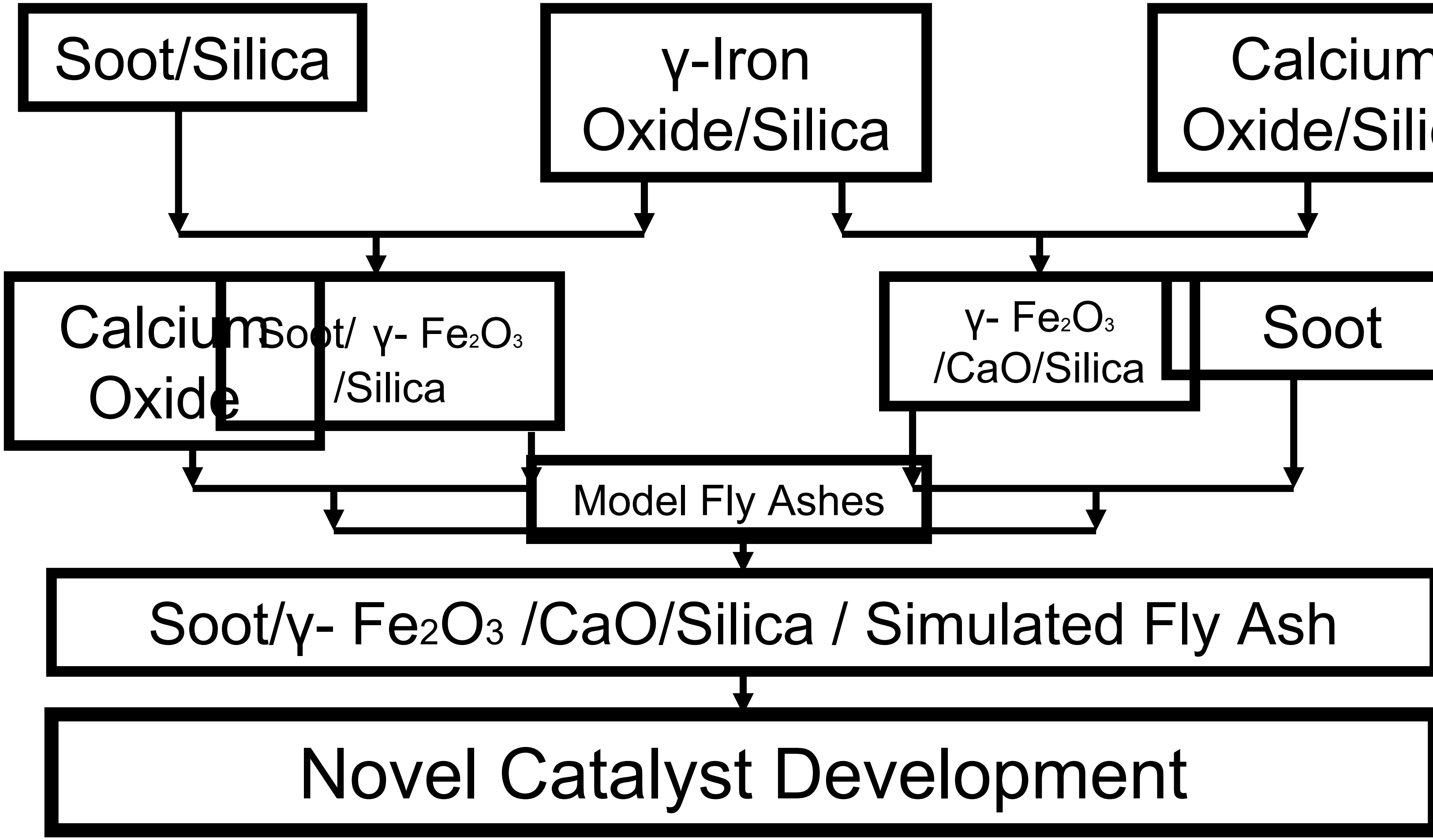


Elemental Analysis

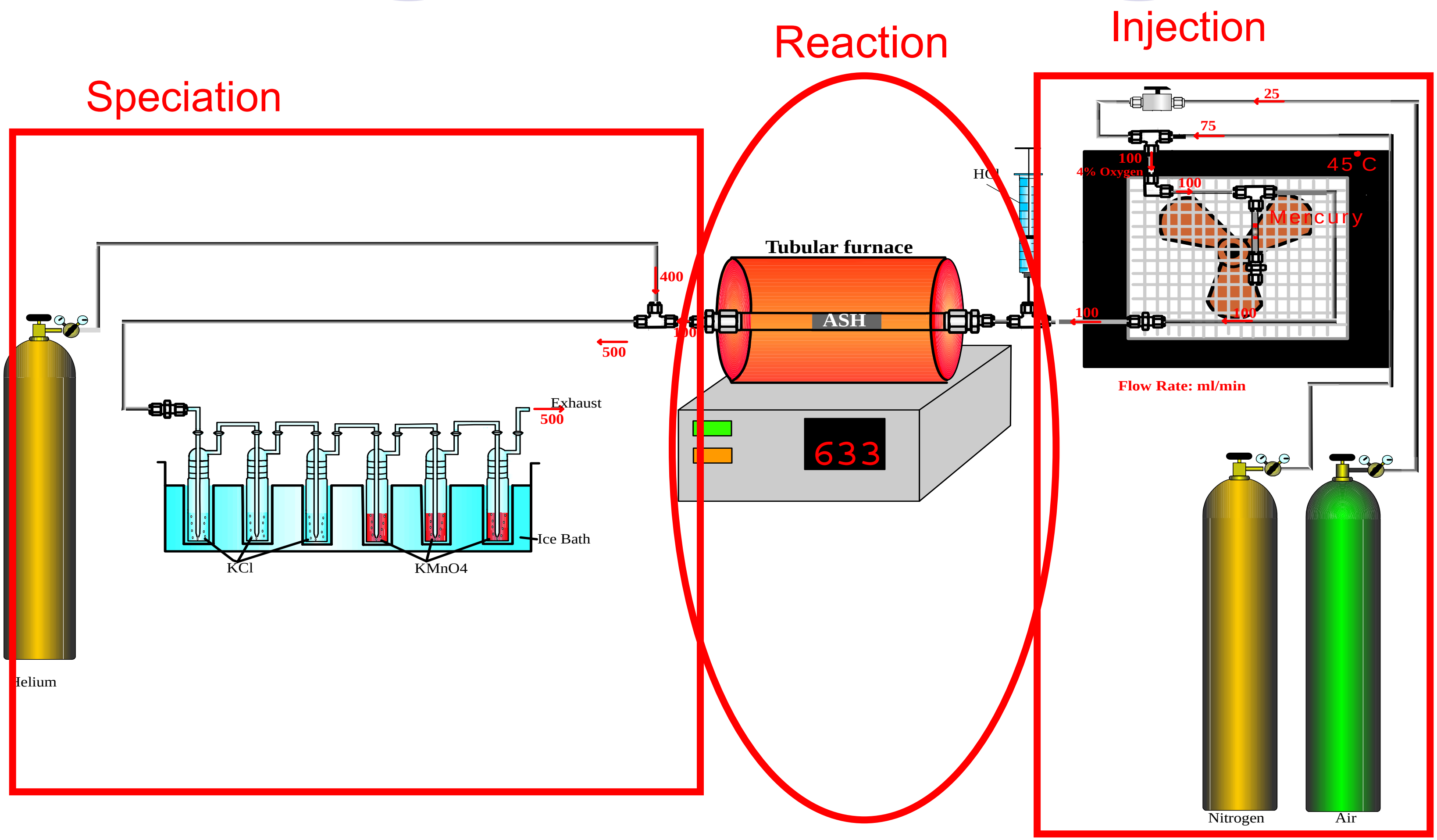
ASH	C (extract)	C (unextract)	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	O	Surface Area (m^2/g)
1	0.07	13.23	0	0.27	14.14	26.91	0.4	2.8	0.77	1.26	5.41	48.05	6.98
2	0.24	2.93	0	0.6	15.9	27.01	0.45	2.59	0.92	0.77	3.05	48.7	2.62
3	0.025	4.04	0.45	0.71	14.13	26.76	0.26	3.11	2.16	1.32	3.26	47.85	2.35
4	0.01	0.95	1.83	2.81	10.01	19.86	0.75	0.89	15.21	1.18	3.69	43.77	0.95
10	0	0	1.45	0.45	11.9	20.71	1.08	1.64	2.58	0.55	16.58	43.07	0.54

- Ash1 has high carbon content and also high surface area
- Ash 4 has high calcium and magnesium content and low carbon and a very low surface area
- Ash 10 has high iron content with negligible carbon and very low surface area. According to IR analysis, Ash 10 has both iron oxide and iron aluminum silicates
- Based on the elemental analysis of fly ashes; carbon, calcium and iron were considered the major components of the fly ashes and model fly ashes were designed on these compounds and silica as the base compound

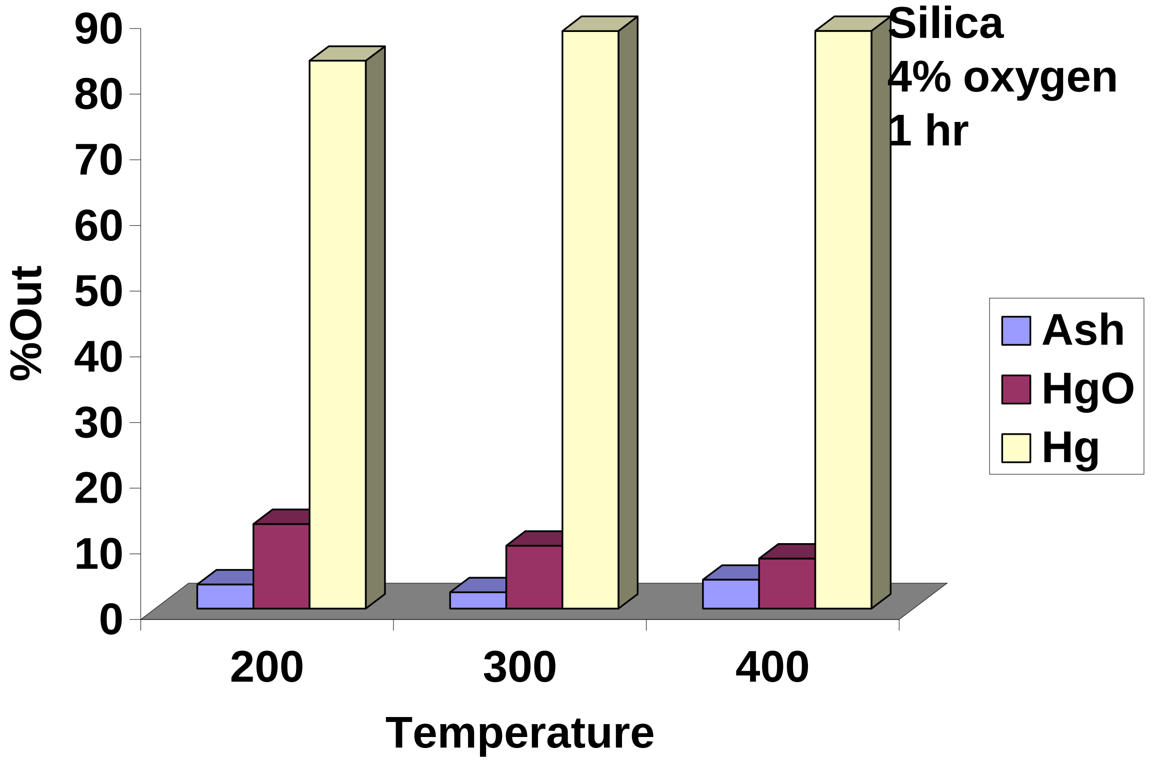
Experimental Approach: Surface



Experimental Setup



Selection of inert material



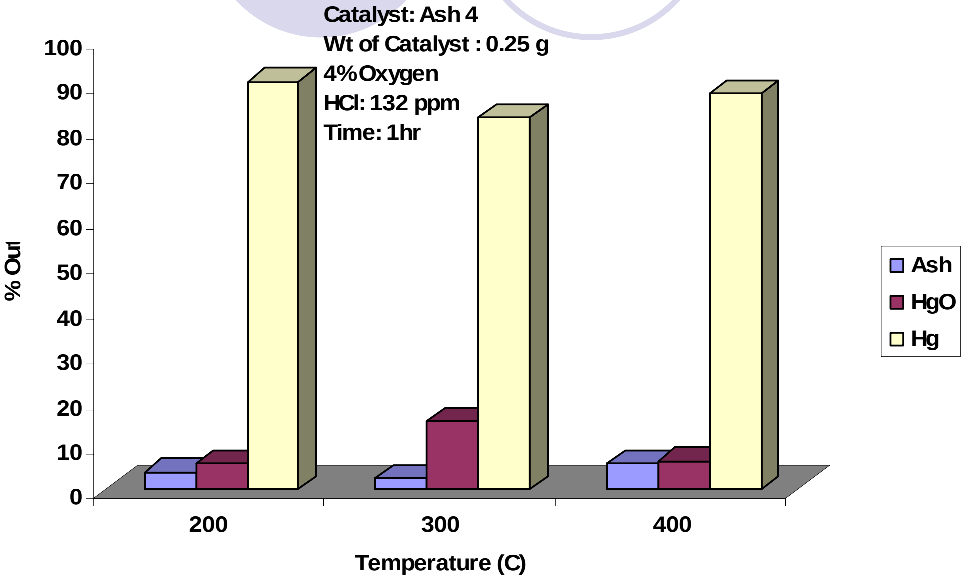
Surface Catalyzed Transformations: Importance of HCl

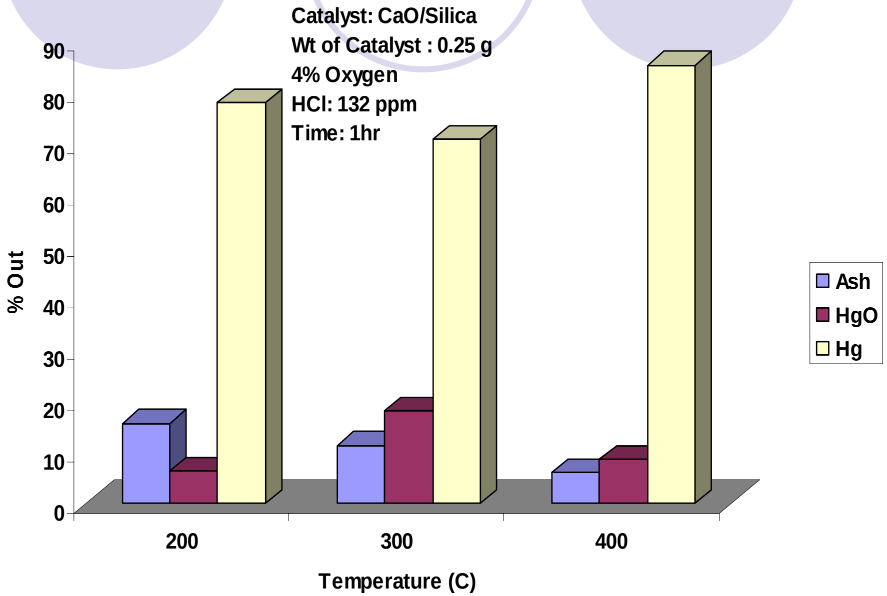
- HCl not a good oxidizing agent
- But in the presence of surface it is converted to chlorine: Deacon Reaction

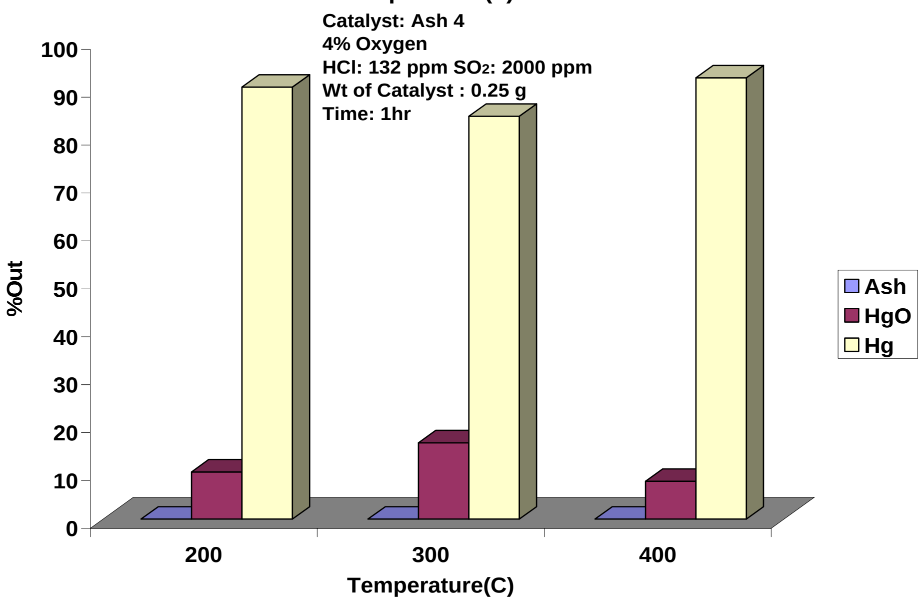
$$2HCl + 2O_2 \longrightarrow H_2O + Cl_2$$

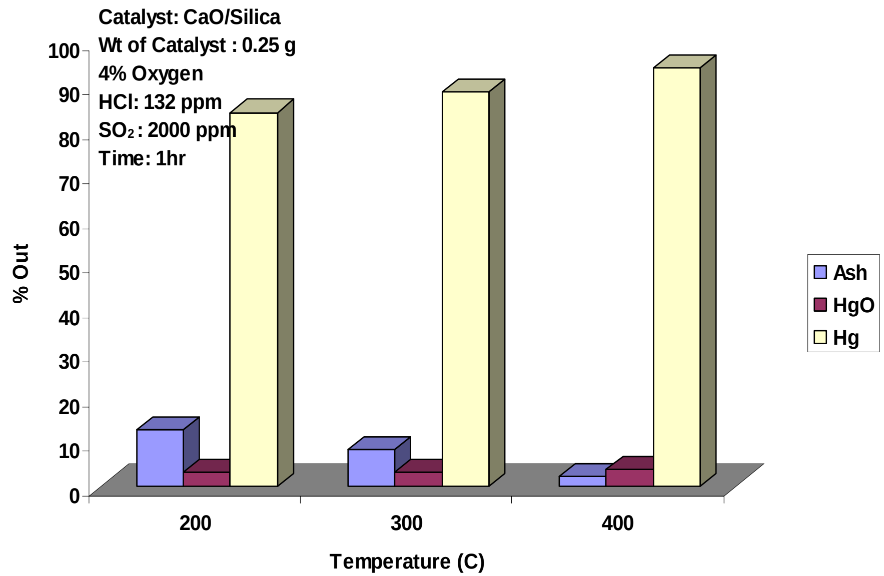
- Chlorine better oxidizing agent.
- Effect of HCl on mercury oxidation/chlorination in the presence of fly ash

Co-relative analysis: Presence of Calcium Oxide

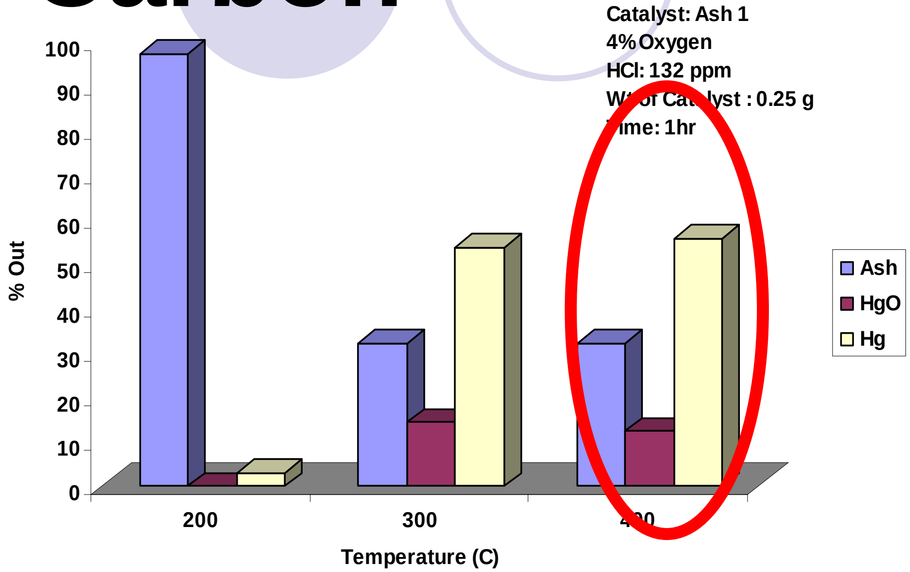


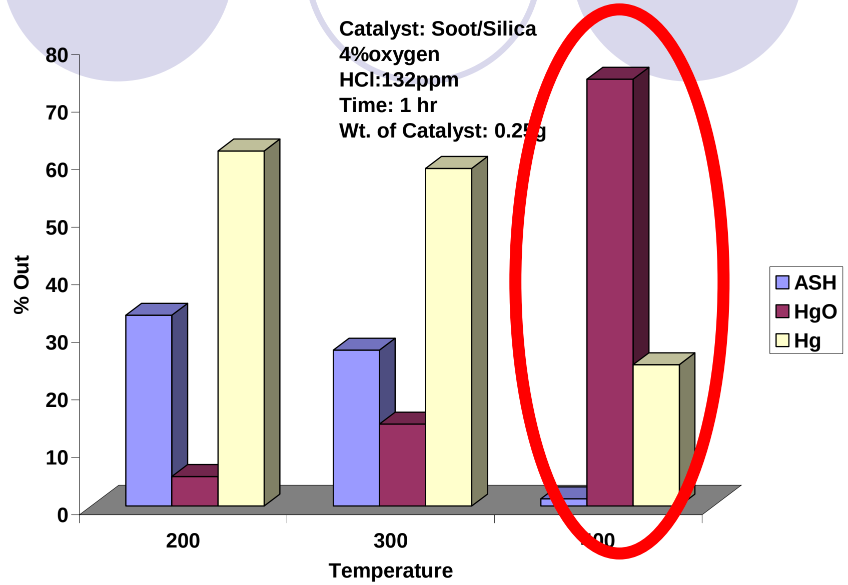


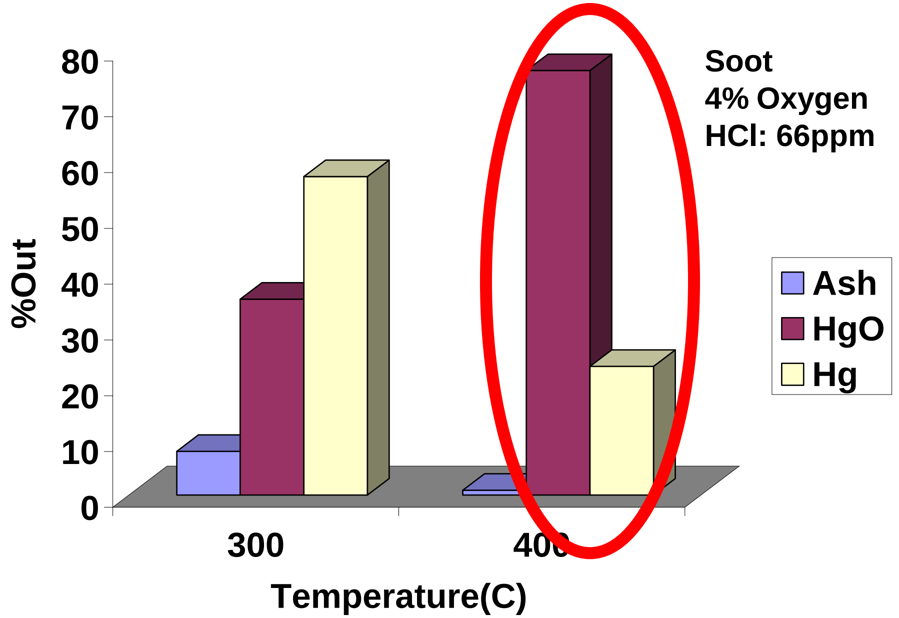




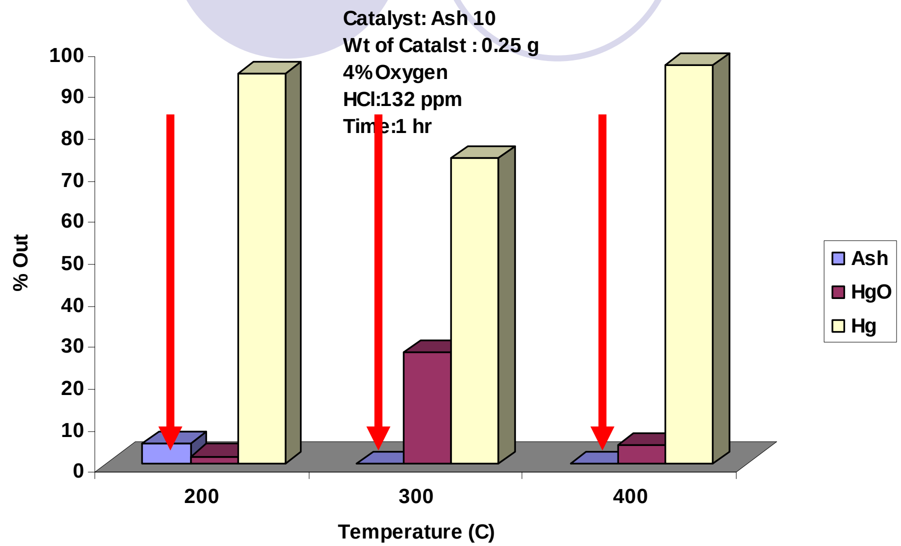
Co-relative analysis: Presence of Carbon

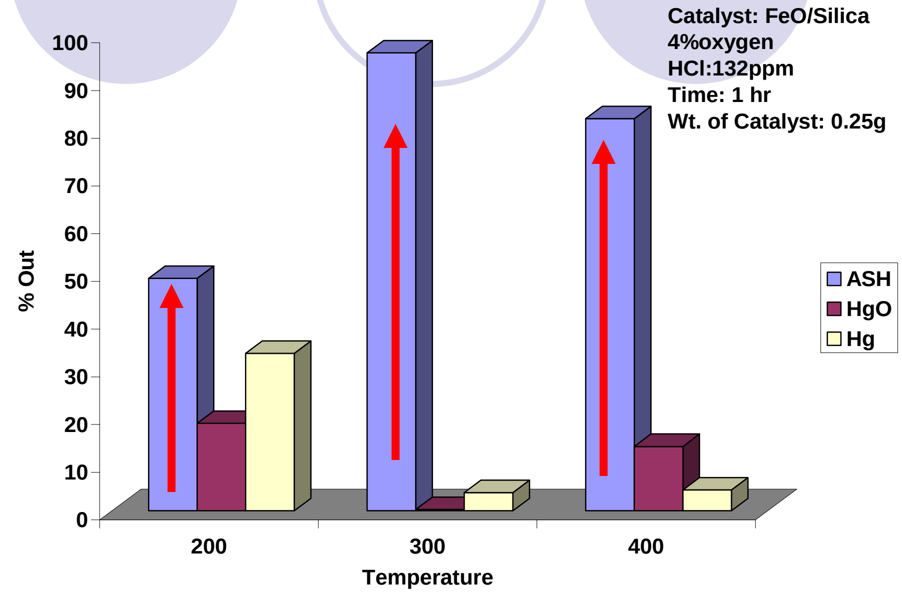


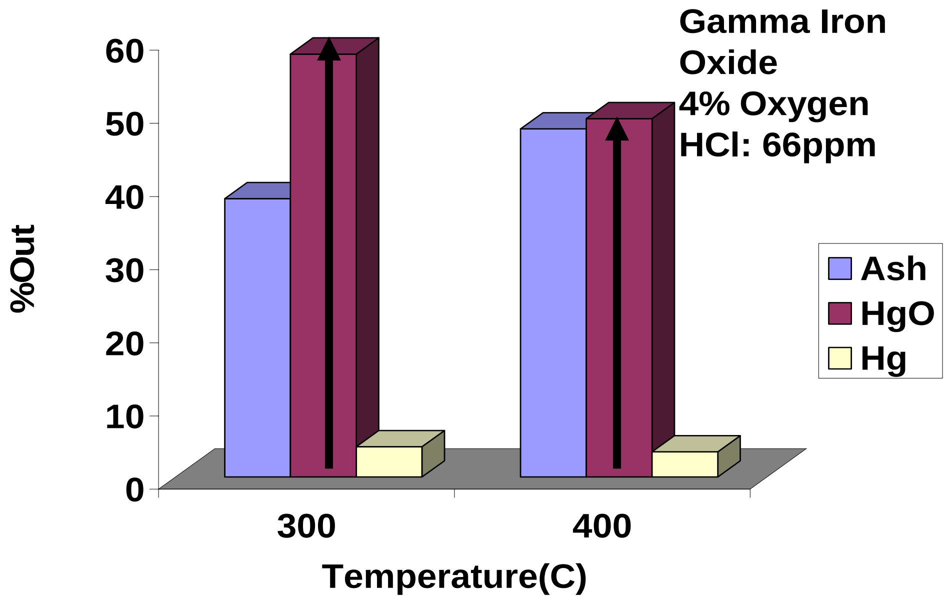




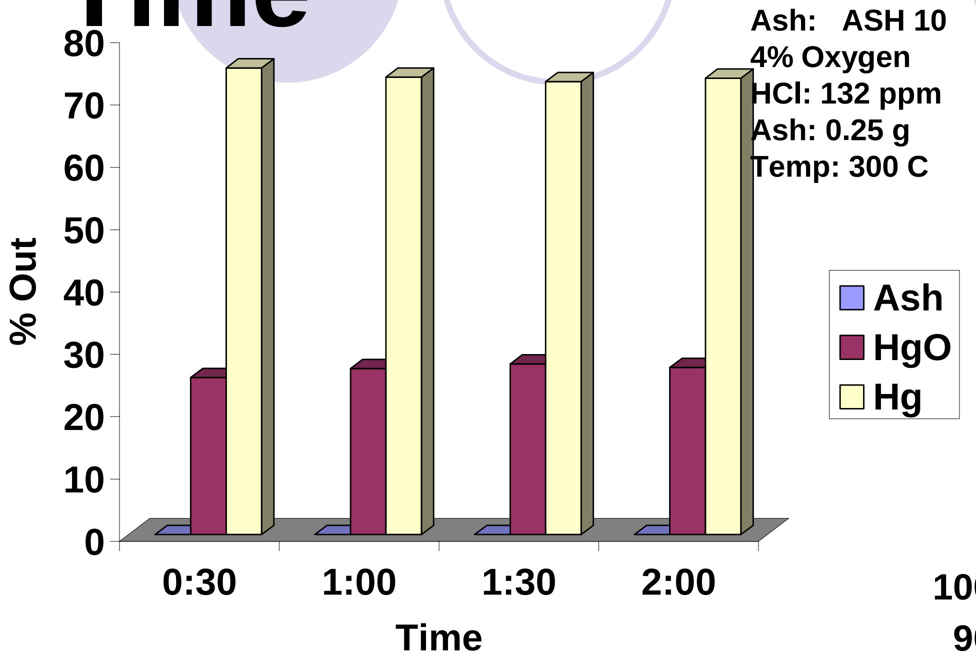
Co-relative analysis: Presence of Iron Oxide

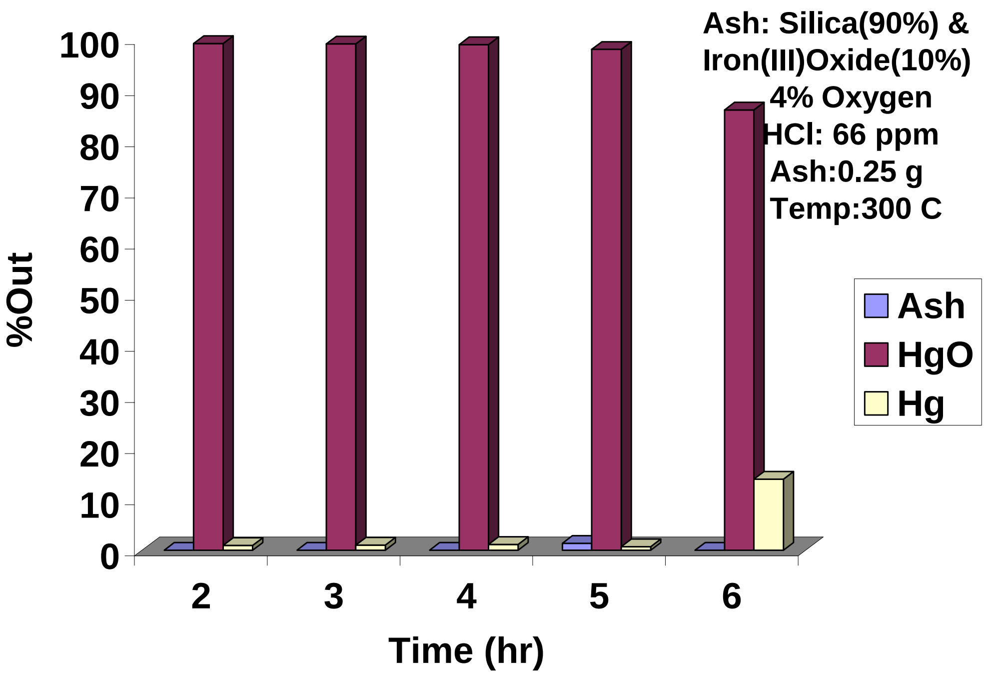






Co-relative analysis: Effect of Time

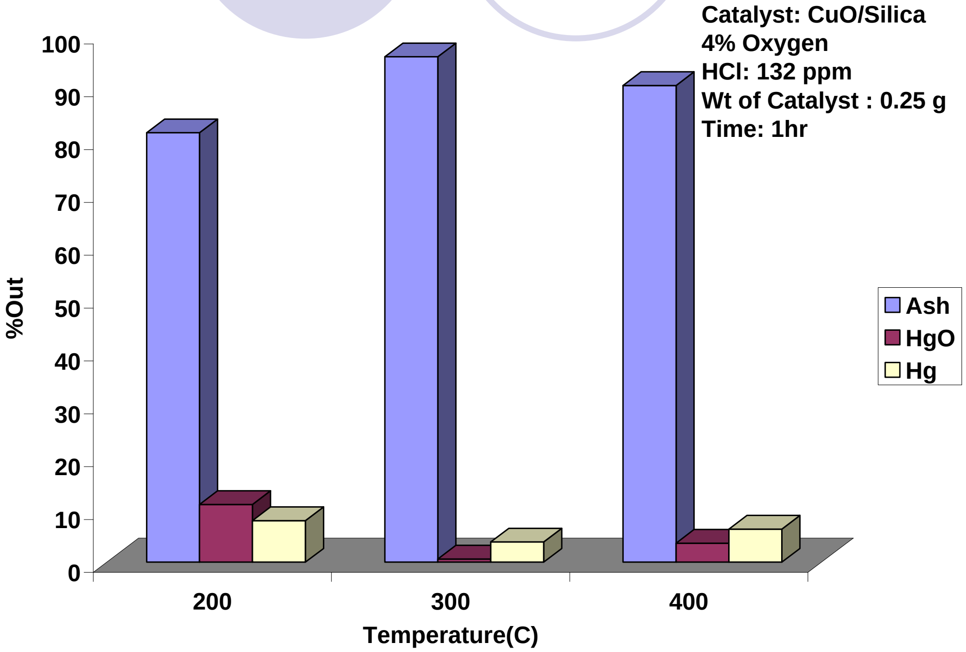


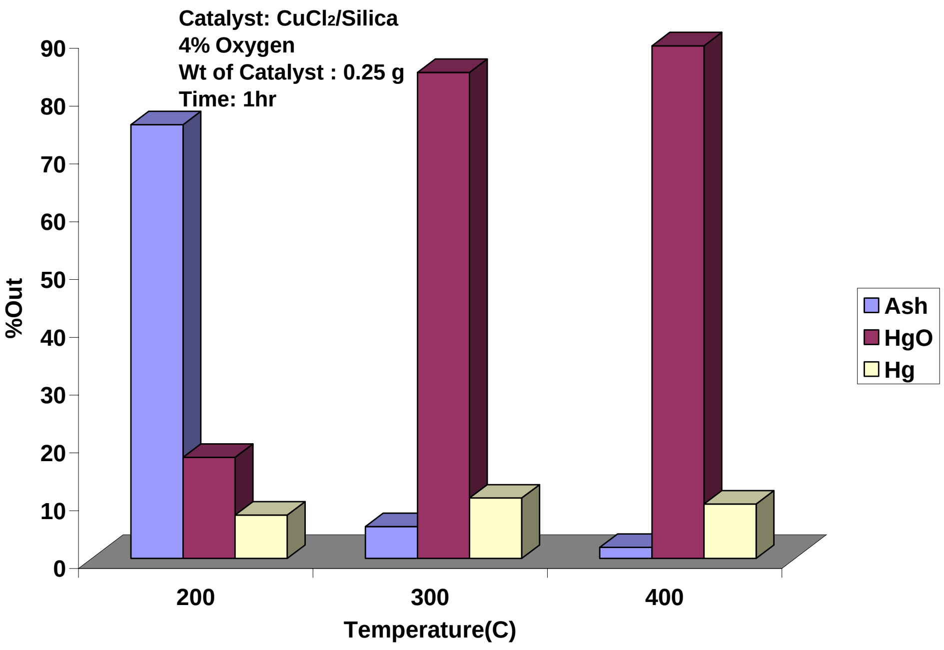


Conclusions-I

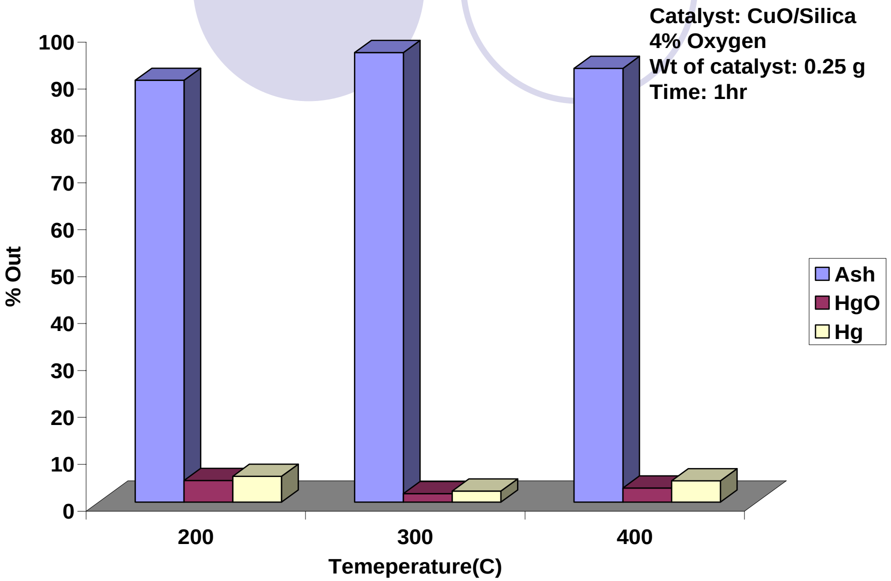
- HCl is a very good oxidizing agent
- Amount of adsorption depends on the surface area and surface composition
- Adsorption of mercury and chlorine in close vicinity is very important for mercury chlorination
- Potent metal oxides necessary for mercury oxidation? What is the real key component?

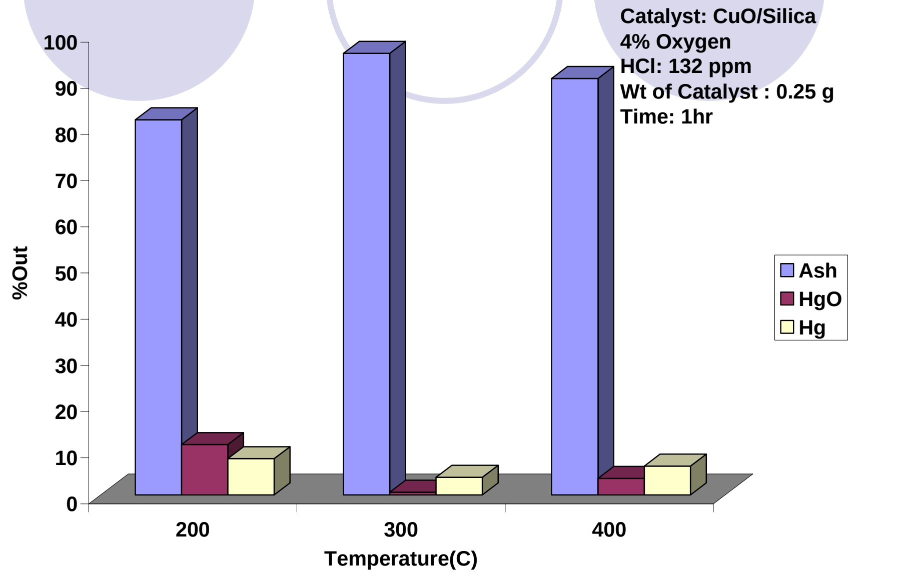
Surface Catalyzed Transformations: Presence of Copper and Chlorine

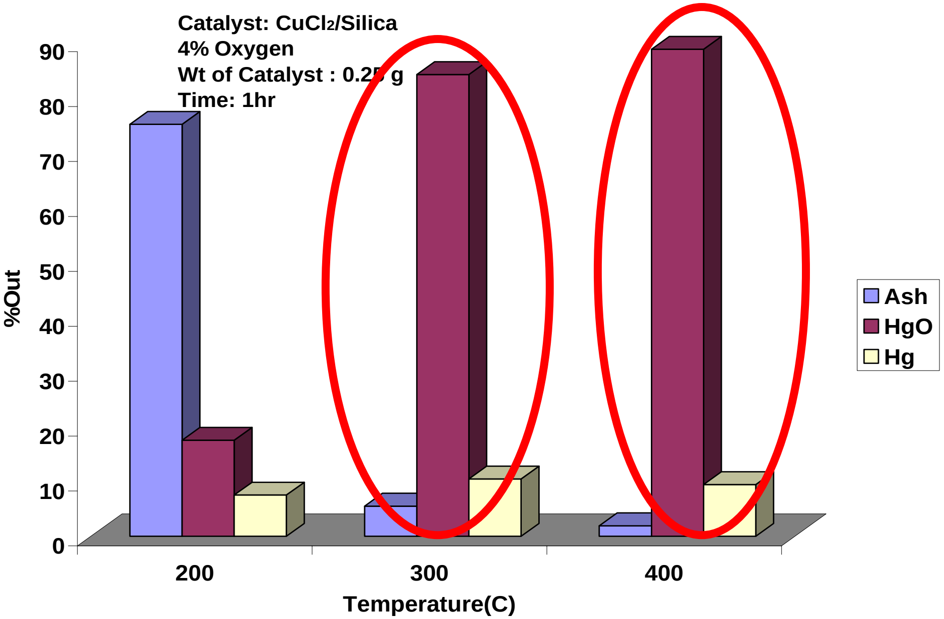


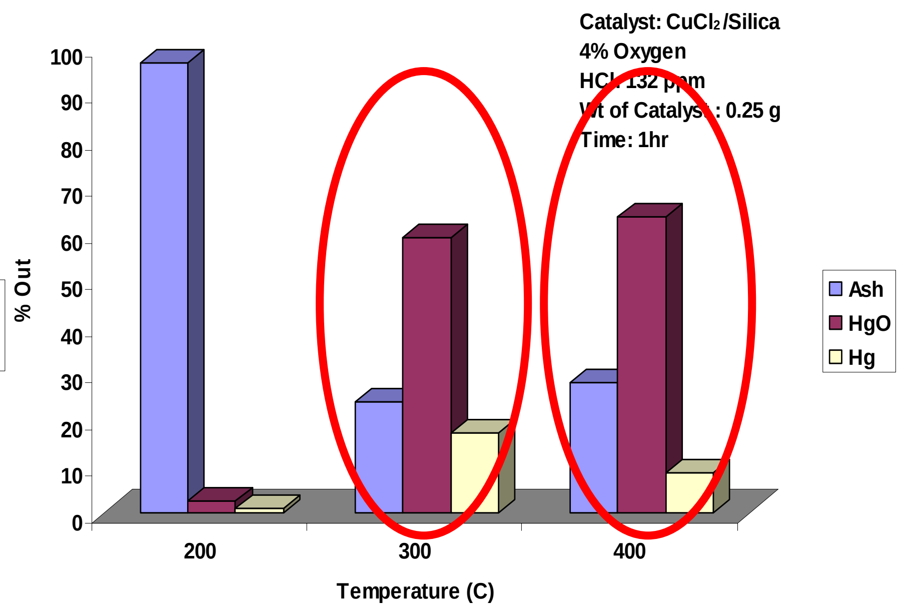


Surface Catalyzed Transformations: Presence of Copper Oxide and Copper Chloride

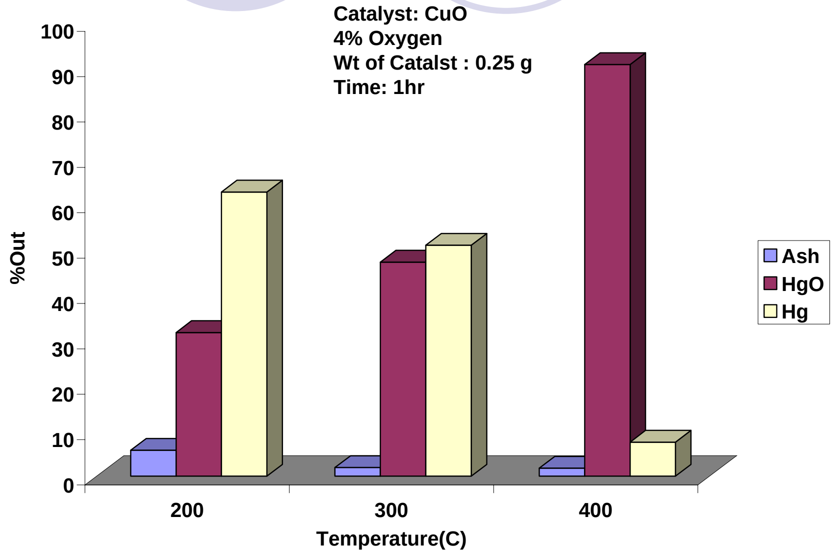


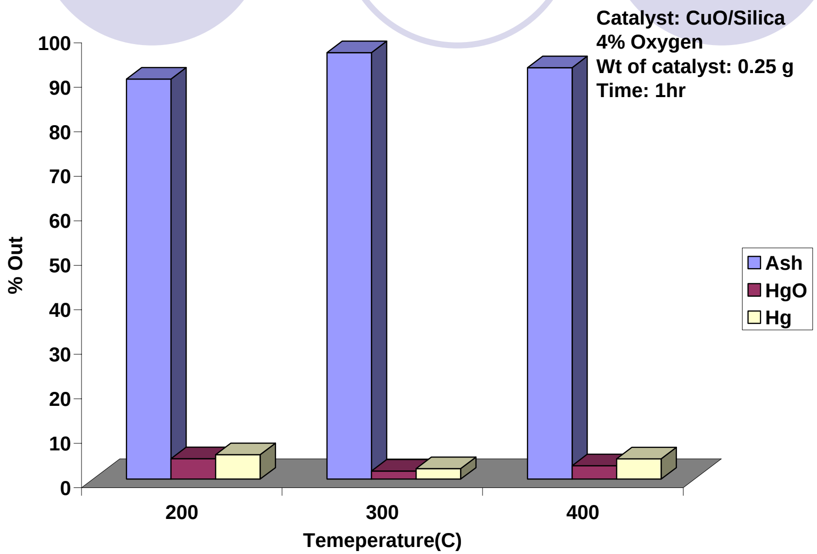


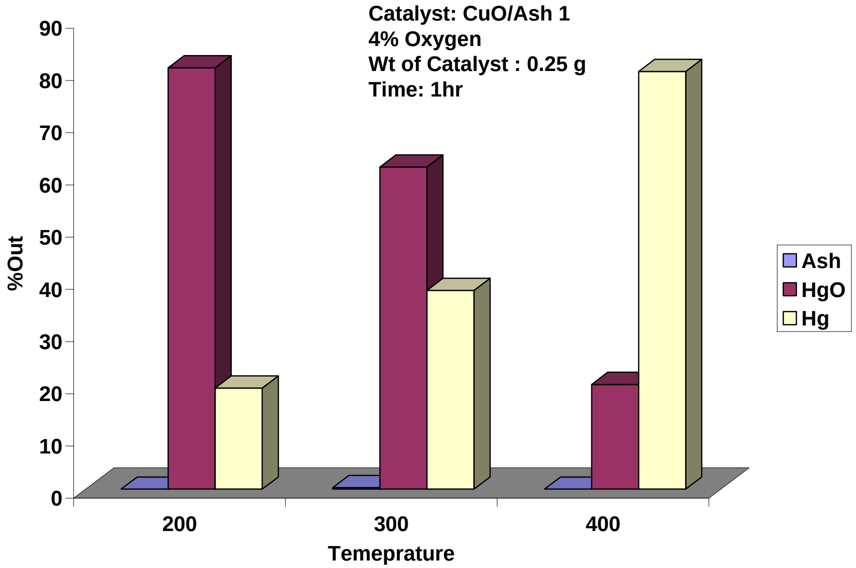


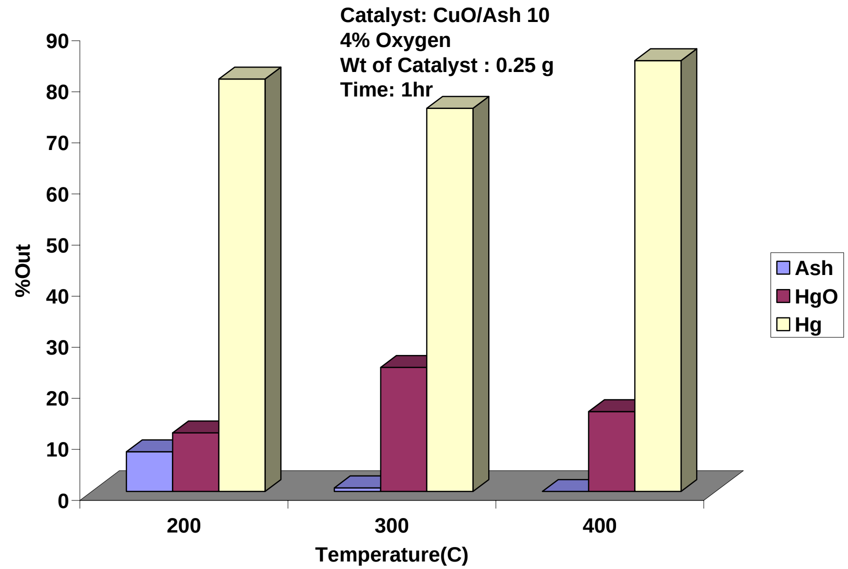


The real key component : Copper Oxide?

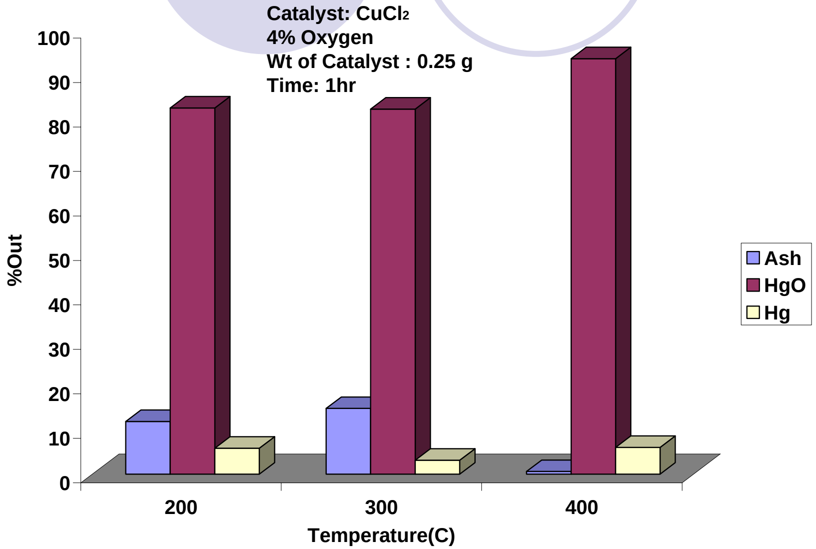


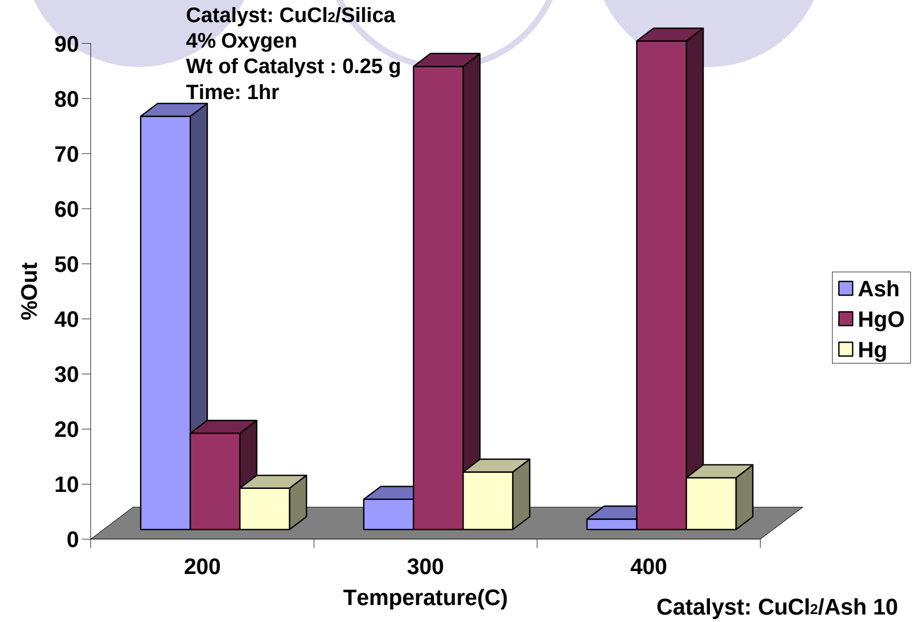


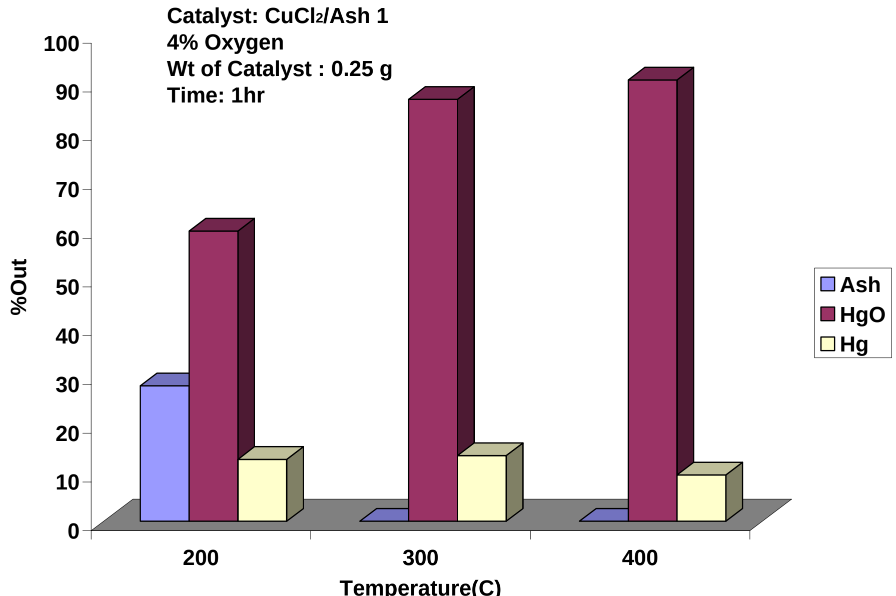


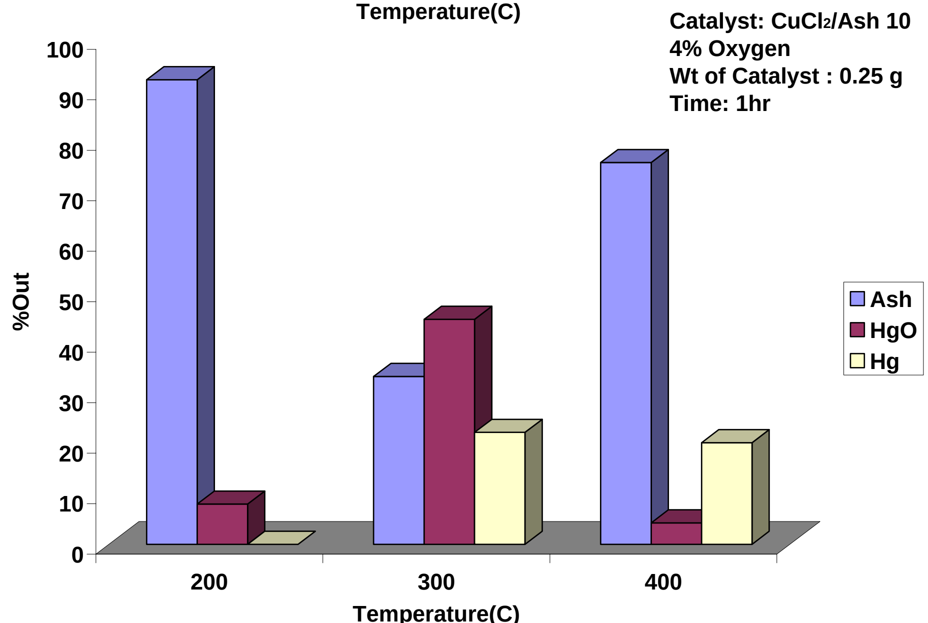


The real key component: Copper Chloride?









Conclusions

- Calcium oxide is neither adsorbs nor oxidizes mercury
- Soot shows lower adsorption than the unburnt carbon present in the fly ash, in spite of its high surface area.
- The form of Iron Oxide has a major effect on adsorption/oxidation of mercury
- HCl is a very good oxidizing agent for mercury.
- Chlorine present as metal chloride is much more effective oxidizing agent
- The real key component in the fly ash is determined by not only the strongest oxidizing component of the fly ash but the gas phase composition and conditions.

Acknowledgement

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